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Inherent Photoluminescence Properties of Poly(propyl ether imine) Dendrimers

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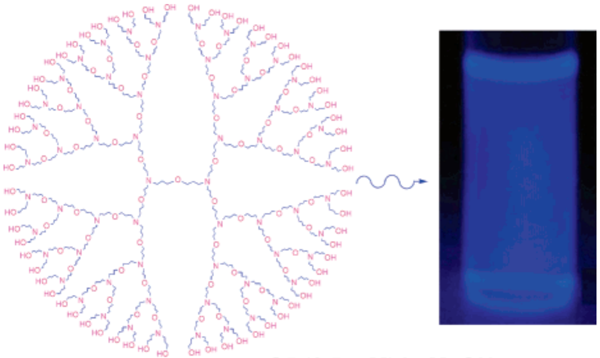
ABSTRACT



G5 (0.5 mM) in MeOH

Hydroxyl group terminated poly(propyl ether imine) dendrimers of 1 to 5 generations absorb in the region of 260–340 nm, in MeOH and aqueous solutions. Excitation of a solution of the dendrimers at 330 nm led to an emission at ∼390 nm. The emission intensities increased under acidic pH and in more viscous solvents. The presence of air did not affect the emission profiles, as also aging of a dendrimer solution for prolonged periods. Lifetime measurements show at least two species responsible for the emission. Anions perchlorate, periodate, nitrite, and pyridinium methyliodide quenched the fluorescence efficiently, among several anions tested.

Dendrimers present a number of molecular and supramolecular features, as a result of their unique architecture.[1] An anomalous property of luminescence has been reported for dendritic macromolecules in recent years.[2−5] The origin of the luminescence in nonfunctionalized dendrimers, such as the carboxylic acid terminated poly(amido amine) (PAMAM) dendrimers and amine terminated poly(propylene imine) (PPI) dendrimers and hyperbranched poly(amino esters), is not fully understood at present. Following these reports, we studied the recently established poly(propyl ether imine) (PETIM)[6] dendrimers for their luminescence behavior. In the event, we observe that these new types of dendrimers exhibit luminescence properties. The details of the studies are presented herein.

PETIM dendrimers are constituted with an amine as the branching moiety and an ether as the linker, interconnected by propylene spacers. The dendrimers are synthesized by divergent synthesis and dendrimers up to six generations, presenting 128 peripheral functionalities, have been synthesized.[6,7] Molecular structures of the hydroxyl-group terminated PETIM dendrimers utilized in the luminescence studies are presented in Figure 1.

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(1) Many aspects of dendrimer chemistry are covered in: (a) *Top. Curr. Chem*. **1998**, *197*, 1−228. (b) *Top. Curr. Chem*. **2000**, *210*, 1−308. (c) *Top. Curr. Chem*. **2001**, *212*, 1−194. (d) *Top. Curr. Chem*. **2001**, *217*, 1−238. (e) *Top. Curr. Chem*. **2003**, *228*, 1−258. (f) *Dendrimers and Other Dendritic Polymers*; Fréchet, J. M. J., Tomalia, D. A., Eds.; Wiley: Chichester, UK, 2001.

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10.1021/ol702635w CCC: $40.75

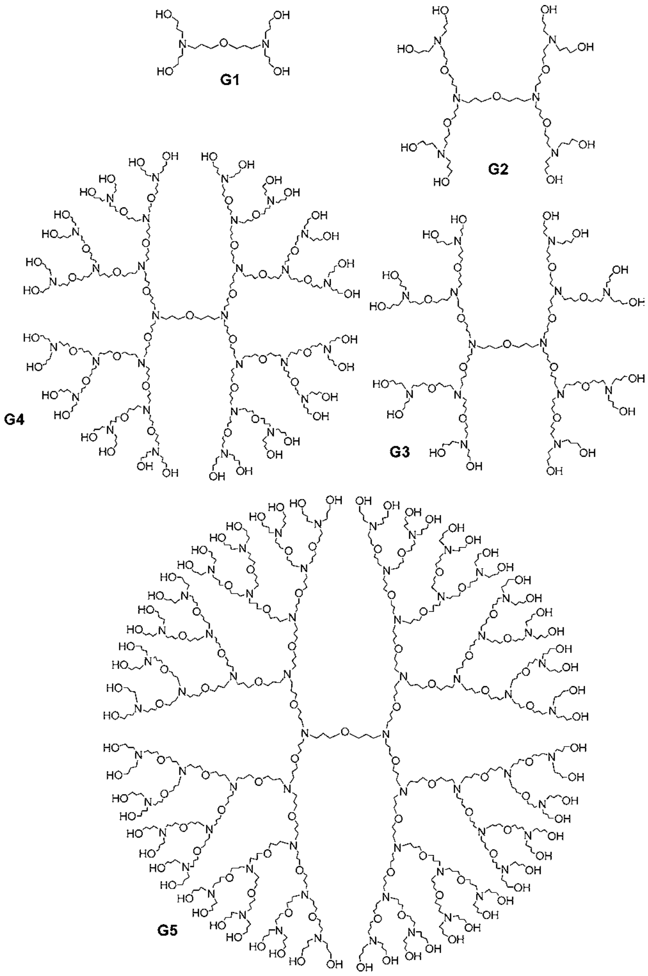

Figure 1. Molecular structures of **G1−G5** PETIM dendrimers.

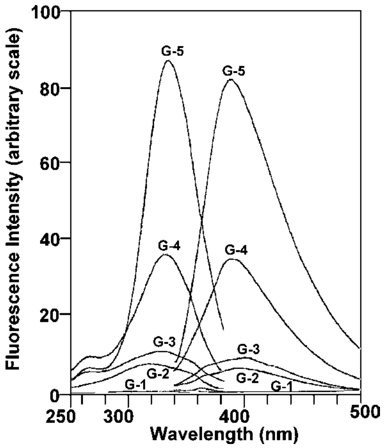

Figure 2. Emission and excitation spectra of PETIM dendrimer generations in MeOH (0.5 mM). $\lambda_{ex} = 330$ nm.

Studies of the dendrimers were conducted in MeOH and aqueous solutions. To achieve equilibrations, the solutions were kept at room temperature for 24 h prior to the studies. The UV−vis spectra were recorded first and it was found that the dendrimers exhibited a broad absorption in the region of 260−340 nm. The lower generation dendrimers were found to require higher concentrations of the solutions than the higher generation dendrimers, for equivalent absorption intensities.

Luminescence studies were carried out in MeOH and aqueous solutions, at submillimolar concentrations. In early studies, it was found that excitation of a methanolic solution of the dendrimers at 273 nm provided a weak emission band at ∼310 nm. The **G4** and **G5** dendrimers had shown, in addition, an emission band at ∼390 nm. This additional band at ∼390 nm was found to occur above 0.06 mM only. On the other hand, excitation of the solution at 330 nm led to an emission band at ∼390 nm (Figure 2). The emission band at ∼390 nm was seen consistently for **G2−G5** generations studied. The corresponding excitation spectra were also analyzed and the excitation spectra showed λ_{max} at ∼330 nm. A weak excitation band at ∼270 nm was also observed for the **G3−G5** dendrimers. These general observations of emission from these dendrimers in MeOH solutions could be repeated for several batches of dendrimer preparations.

Concentration-dependent studies were followed and it was found that the emission intensities of the dendrimers increased with increasing concentrations of the solutions in MeOH. An examination of the above observations agreed with the fluorescence properties emanating from PPI and PAMAM dendrimers, reported previously.[2−4]

The absorption spectral profiles of aqueous solutions of dendrimers were found to be similar as in methanolic solutions, except the emission intensities were considerably lower. The experiments were conducted in detail[8] for the **G3** dendrimer in aqueous solutions. The emission profiles were assessed at various pH values of the solution, adjusted either with aq HCl solution or aq NaOH solution. Figure 3

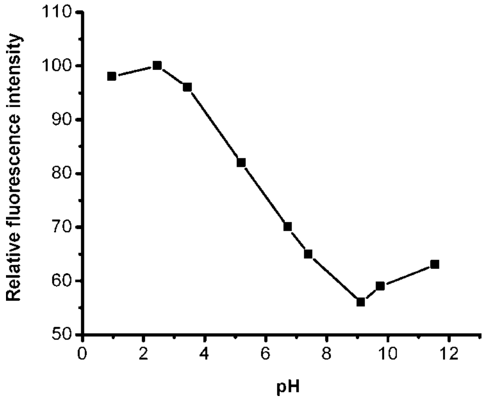

Figure 3. Fluorescence intensities of aqueous solutions of the **G3** dendrimer (0.4 mM) at different pH values.

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shows the effect of pH on the fluorescence intensity at 390 nm of the dendrimer solutions. The emission intensity at 390 nm ($\lambda_{ex} = 330$ nm) was found to increase dramatically from the neutral to the acidic pH and attained a maximum value at pH ~2.4. The alkaline pH solutions did not show such a difference in the emission band intensity. Thus, protonation of the tertiary amines resulted in increased emission intensities. A temperature-dependent study was conducted with an aqueous solution of **G4** dendrimer between 10 and 60 °C and it was observed that the intensity did not differ significantly in this temperature range.

An effort to assess the fluorescence efficiency was undertaken. Accordingly, the quantum yields (Φ) were measured for all the dendrimer generations in MeOH solutions, by a relative method, for which 2-aminopyridine ($\Phi = 0.6$) acted as the reference.[9] From these measurements, the percentage Φ were found to be **G2** 0.4, **G3** 0.43, **G4** 0.56, and **G5** 0.96. The measured quantum yields showed a trend of increasing Φ values with increasing generations.

Solutions in ethylene glycol (EG) and diethylene glycol (DEG) were also tested. For this purpose, **G4** dendrimer was chosen. It was found that the emission intensities increased for both solutions, in comparison to MeOH and aqueous solutions. It was found further that both EG and DEG solutions exhibited significantly increased emission intensity upon storage for several weeks. The increased emission intensities in the above solvents may be related to the dependence of the intensities on the viscosities of the solvents. The conventional solvent-dependent effects, wherein the emission spectral wavelengths would shift considerably, depending on the solvent for a given fluorophore, could not be observed in the dendrimers studied.

It was also found that an aqueous solution of dendrimer purged with air and maintained at 0 °C, room temperature, and 50 °C for over 45 days did not cause a change in either λ_{em} or the intensities.

The emission behavior of a thin film was measured. A thin film of the **G3** dendrimer was observed to have profiles similar to that in solution. The observation from solid state measurements reiterates the solution phase behavior that fluorescence is inherent to the dendrimers.

A number of amine and hydroxyl group containing compounds that possess groups similar to that present in dendrimers were tested. These compounds included D-glucose, 2,2′-bis(hydroxymethyl)-1,3-propanediol, glycerol, triethanol amine, tripropanol amine, *N*-methylpyrrolidine, *N*,*N*′-dimethylaminotris(hydroxymethyl)methane, *N*-(3-hydroxypropyl)-pyrrolidine, and (2*S*)-2-hydroxymethyl-1-(γ-hydroxypropyl)-pyrrolidine. None of these compounds exhibited emission in the wavelength ranges tested for the dendrimers.

Studies were continued further to identify the species associated with the emission. The lifetime measurements were thus undertaken. An excitation wavelength of 267 nm was obtained from the third harmonic generator using an Nd:YAG laser source and the emission decay was monitored at 390 nm.[10] There were three distinct lifetimes for the **G2**−**G5** dendrimers. The measured lifetimes (τ) and the fractional intensities (α) for **G2**−**G5** are presented in Table 1. Further analysis showed that the τ_1 value was observed common for the samples as well as the blank solvent, at the sensitivity used for data collection. In light of this, the τ_1 component could be ascribed to be due to the background emission of the solvent. On the other hand, the presence of the remaining two lifetimes indicates either a single fluorescent moiety within the dendritic structure leads to two distinct microenvironments, or two different fluorescent moieties with different lifetimes emerge from the dendritic molecules. It is noted that the τ_3 of ~7 ns is seen for other dendrimers reported previously.[2,4,5,11] While differences in the lifetimes across various generations of dendrimers could not be observed, differences due to the solvent system were seen. Thus, MeOH solutions showed higher lifetimes than aqueous solutions.

Table 1. Measured Emission Lifetimes (τ) and Fractional Intensities (α) of **G2**−**G5** Dendrimers.

solvent	τ_1 (α_1)	τ_2 (α_2)	τ_3 (α_3)
MeOH	0.34−0.50 ns (0.26)	1.32−2.08 ns (0.42)	6.46−7.31 ns (0.32)
H_2O	0.14−0.25 ns (0.23)	1.33−1.90 ns (0.29)	5.22−6.98 ns (0.48)

It is pertinent to compare the emission behavior of PETIM with that of the PPI dendrimers, as PETIM dendrimers may be considered to incorporate additional oxygen atoms in a PPI-like dendrimer molecular structure. Significant differences in the emission profiles between PPI and PETIM dendrimers are (i) $\lambda_{ex} = 430$ nm and $\lambda_{em} = 465$ nm for PPI and λ_{ex} 330 nm and $\lambda_{em} = 390$ nm for PETIM, and (ii) the emission intensity of PPI dendrimers increases considerably upon exposure to air, whereas the PETIM dendrimers are unaffected by air. It was rationalized that "an oxygen-interacted moiety with the tertiary amines" is the most probable cause for the evolution of fluorescence in the PPI series of dendrimers.[4b] The reduced λ_{ex} and λ_{em} in the case of PETIM dendrimers is accountable for the molecular constitution. The inability of PETIM dendrimers to have an effect induced by air indicates a role for the oxygen atoms that abound in the dendritic structure. Thus, it is likely that an oxygen interaction with tertiary amines exists within the dendritic structure and such an interaction precludes an effect by oxygen from an external source.

Following the studies presented above, the influence of the inorganic anions on the emission behavior of the dendrimers was studied. The preliminary study was undertaken to identify the effect of quenchers on the inherent dendrimer fluorescence. In this instance, several inorganic anions were chosen, as the quenching efficiencies of inorganic anions are known extensively.[12] The effect of inorganic anions on the fluorescence property was tested

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(8) Aqueous solutions of the dendrimers (0.4 mM) have pH 9.4−9.7.

(9) Rusakowicz, R.; Testa, A. C. *J. Phy. Chem*. **1968**, *72*, 2680−2681.

(10) The lifetimes were found to be the same when $\lambda_{ex} = 330$ nm, obtained through nanosecond flash lamp, was used.

(11) Zheng, J.; Petty, J. T.; Dickson, R. M. *J. Am. Chem. Soc*. **2003**, *125*, 7780−7781.

specifically for the **G5** dendrimer. The experiment was conducted by the addition of aliquots of various inorganic anions, from a stock solution, to a solution containing the dendrimer. The concentration range of the inorganic anions was maintained up to 0.02 M. The classic Stern−Volmer plots were used to describe the observed effect of the intrinsic fluorescence of dendrimers upon addition of the inorganic anions (Figure 4). Of several anions, it was observed that $NaIO_4$, $(NH_4)_2S_2O_8$, $NaNO_2$, $AgClO_4$, and pyridinium methyliodide quenched the fluorescence of the dendrimer efficiently. A significant variation in the quenching constants, as well as the bimolecular quenching rates, was observed for these anions, when compared to the remaining anions. An indication of a slightly upward curvature of the quenching in the case of $NaIO_4$ and $(NH_4)_2S_2O_8$ indicated that the fluorescence quenching by these anions might be due to a static quenching. Such a static quenching, in turn, would require the quencher placing itself in the vicinity of the excited state of the fluorophore. It is probable that the larger anions, namely, $NaIO_4$ and $(NH_4)_2S_2O_8$, reside at the interior of the dendritic framework, provided the excited fluorophore originates at the interior of the dendrimer. On the other hand, $NaNO_2$ and pyridinium methiodide are likely to encounter an energy transfer, due to the presence of absorption components around 400 nm with these salts. The study shows the possibility of utilizing the fluorescence quenching to develop dendrimer-based sensors for anions.

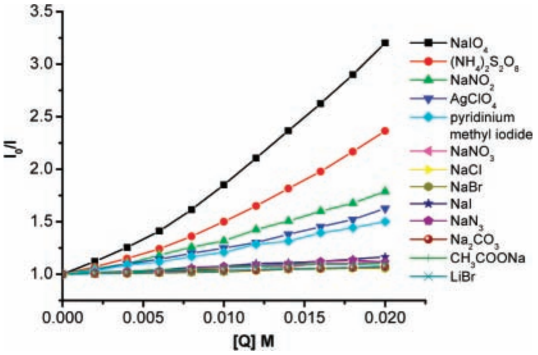

Figure 4. The Stern−Volmer plots of G5 dendrimer in aqueous solution (0.1 mM), in the presence of various inorganic salts ($\lambda_{em} = 390$ nm; $\lambda_{ex} = 330$ nm).

Table 2. Quenching Parameters Obtained from Steady-State Emission of the **G5** Dendrimer.

anion	K_{s-v} (mol^{-1})	K_q (mol^{-1} S^{-1})
$NaIO_4$	111.95	16.04×10^9
persulfate	68.76	9.85×10^9
$NaNO_2$	39.78	5.70×10^9
$AgClO_4$	30.38	4.35×10^9
pyridinium methiodide	25.29	3.62×10^9
NaI	8.37	1.20×10^9
NaN_3	6.75	9.7×10^8
$NaNO_3$	6.41	9.2×10^8
CH_3COONa	5.33	7.6×10^8
LiBr	3.91	5.6×10^8
Na_2CO_3	3.73	5.3×10^8
NaBr	3.33	4.7×10^8
NaCl	2.91	4.2×10^8

In conclusion, the anomalous fluorescence arising from PETIM dendrimers is established through a series of experiments. The anomalous emission profile may arise through a moiety having the tertiary amine interacting with the oxygen, as envisaged previously for the PPI dendrimers.[4b] Such a moiety would involve the oxygen in-built within the PETIM dendrimers. In addition, altered hydrogen-bonding properties of the dendrimers could also contribute. The influence of hydrogen bonding on the luminescence is known for amines in general.[13] The quenching of the fluorescence originating from the PETIM dendrimers by inorganic anions has also been established in the present study.

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Supporting Information Available: Fluorescence spectra, thin-film spectra, variable-temperature spectra, spectra of samples purged with air and nitrogen, lifetime values at λ_{ex} 330 nm, and experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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